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Effects of concentration and temperature on the coupled Heat and mass transport in liquid mixtures

Abstract

Using published experimental data on the thermal conductivity, mutual diffusivity, and heats of transport, the degree of coupling between heat and mass flows has been calculated for binary and ternary nonideal liquid mixtures. The binary mixtures consist of two types: the first is six systems of six-to-eight-carbon straight and branched chain alkanes in chloroform and in carbon tetrachloride; and the second is mixtures of carbon tetrachloride with benzene, toluene, 2-propanone, n-hexane, and 11-octane. The ternary mixture considered is toluene-chlorobenzene-bromobenzene. The published data are available at 25°C, 30°C, 35°C and ambient pressure. Using the linear nonequilibrium thermodynamics (LNET) and the dissipation-phenomenological equation (DPE) approach, the effects of concentration, temperature, molecular weight, chain-length, solute, solvent, and branching on the degree of coupling are examined. The extent of coupling and the thermal diffusion ratio are expressed in terms of the transport coefficients to obtain a better understanding of the interactions between heat and mass flows in liquid mixtures. It is found that the composition of the heavy component bromobenzene changes the direction and magnitude of the two-flow coupling in the ternary mixture.

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Introduction

Coupled processes are important in physical and biological systems; examples include separation by thermal diffusion (thermal osmosis) [1], thermoelectric phenomena, and the active transport of a substance coupled to a chemical reaction [3, 3]. Since many chemical reactions within a biological cell produce or consume heat, local temperature gradients may contribute in the transport of materials across the membrane [4]. We can identify the independent flows that can couple by using the dissipation function obtained from the theory of linear nonequilibrium thermodynamics (LNET) based on the Onsager relations [2, 5-7]. This is called the dissipation-phenomenological equations (DPE) approach in which the conjugate forces and flows are used to express the transport and rate processes [8]. The phenomenological equations show the interactions between the various processes through the coupling or the cross-phenomenological coefficients (L_{ij} with $i \neq j$) that are closely related to the transport coefficients. The Onsager reciprocal relations state that these cross-coefficients are equal to each other for the conjugate forces and flows. Once the values for cross-coefficients are known for a system, we can calculate the degree of coupling and their contributions to the rate of entropy production or dissipation.

When we consider a diffusion flow \mathbf{j}_i , and a temperature gradient X_q , which are both the vectors, the cross coefficient L_{qi} is a scalar quantity consistent with the isotropic character of the mixture. Since the coefficients L_i need not to vanish, not only a temperature gradient can cause a heat flux in fluid mixtures, but also an isothermal chemical potential gradient. This latter effect is known as the diffusion thermo effect or the Dufour effect, and is characterized by the heat of transport Q^*_i , which relates the heat flow due to the diffusion of component i under isothermal conditions. Rowley and Horne [9] measured the heat of transport in a carbon tetrachloride cyclohexane mixture, and showed that even though the temperature gradients in initially isothermal liquid mixtures are small, the heat of transport itself may be large. The heat of transport contains information on the actual energy-diffusion relationship of molecular interactions, and has been used for the development of generalized molecular transport models and to obtain information on intermolecular potential wells and mixing rules [10]. The purpose of this study is to examine the effect of concentration, temperature, solvent, solute, and aromatic ring on the coupling for liquid mixtures. To do this a complete set of transport coefficients, which includes the heat of transport, mutual diffusivity, and the conductivity measured at various temperatures is needed. Such data for n-hexane, n-heptane, n-octane, 3-methylpentane, 2, 3-methylpentane, and 2, 2, 4-trimethylpentane in chloroform and in carbon tetrachloride have been reported by Rowley et al. [11,12], and for binary liquid mixtures of carbon tetrachloride with benzene, toluene, 2-propanone, 1-hexane, and 1-octane at various temperatures and ambient pressure by Yi and Rowley [10]. Data for the ternary mixture of toluene-chlorobenzene- bromobenzene are reported by Platt et al. [13, 14]. These transport coefficients are related to the cross-phenomenological coefficients expressing the coupling between heat and mass flows in liquid mixtures.

Heat and mass transfer coupling

For a multicomponent fluid at mechanical equilibrium with negligible body force, and for diffusion based on the mass average velocity, the dissipation function Y is given by [7]

$$\Psi = -\mathbf{J}_q'' \nabla \ln T - \sum_{i,k=1}^{n-1} \mathbf{j}_i a_{ik} \left[\sum_{j=1}^{n-1} \left(\frac{\partial \mu_k}{\partial w_j} \right)_{T,p,w_{i \neq j}} \nabla w_j \right] \geq 0, \quad (1)$$

where $a_{ik} = \delta_{ik} + w_k/w_{ns}$ and δ_{ik} is the unit tensor. The heat flow in the entropy balance equation is \mathbf{J}_q'' and \mathbf{j}_i is the diffusion of component i . For a binary liquid mixture, the independent forces identified from the dissipation function of Eq. (1) for the heat and mass flows are:

$$X_q = -\nabla \ln T, \quad (2)$$

$$X_1 = -\frac{1}{w_2} \left(\frac{\partial \mu_1}{\partial w_1} \right)_{T,p} \nabla w_1. \quad (3)$$

Using these forces we can now establish a set of phenomenological equations for a binary mixture (using $\mathbf{j}_1 = \mathbf{j}_2$)

$$-\mathbf{J}_q'' = L_{qq} \nabla \ln T + L_{1q} \frac{1}{w_2} \left(\frac{\partial \mu_1}{\partial w_1} \right)_{T,p} \nabla w_1, \quad (4)$$

$$-\mathbf{j}_1 = L_{q1} \nabla \ln T + L_{11} \frac{1}{w_2} \left(\frac{\partial \mu_1}{\partial w_1} \right)_{T,p} \nabla w_1. \quad (5)$$

Here \mathbf{j}_i is the diffusion flow of substance 1 in mass per unit area and per unit time relative to the local center of mass, \mathbf{J}_q'' is the second law of heat flow, μ_1 is the chemical Potential of substance 1. From the Onsager reciprocal relations, the matrix of the phenomenological coefficients is symmetric

$$L_{1q} = L_{q1}. \quad (6)$$

The positive value of the dissipation function, Eq. (1), leads to following inequalities for the phenomenological coefficients

$$L_{qq} > 0, \quad L_{11} > 0 \quad \text{and} \quad L_{qq}L_{11} - L_{1q}^2 \geq 0. \quad (7)$$

The coefficient L_{qq} and L_{11} are associated to the thermal conductivity k and the mutual diffusivity D , respectively, while the cross-coefficient L_{1q} or L_{q1} defines the coupling phenomena, namely the thermal diffusion (Soret effect) and the heat flow due to the diffusion of substance i (Dufour effect). These effects are referred to the forces given in Eqs. (4) and (5), however the roles played by the forces and flows are symmetric [6,7]. In principle, each phenomenological coefficient may be measured by a suitable experimental procedure [15]. The heat of transport, Q_i^* of substance 1 is defined as [6][7]

$$Q_i^* = \frac{L_{1q}}{L_{11}} \quad (8)$$

and it can be used in Eqs. (4) and (5) to eliminate the coefficients L_{q1} and L_{1q} . In an isothermal system where $\Delta \ln T = 0$, Eqs. (4) and (5) give

$$Q_1^* = \left(\frac{\mathbf{J}_q''}{\mathbf{j}_1} \right)_T, \quad (9)$$

that is, Q_1^* is the heat carried by a unit diffusion flow of substance 1 when there is no temperature gradient and no diffusion of other substance. The heat of transport in Eq. (9) is based on \mathbf{J}_q'' , and on the diffusion flow referred to the mass average velocity; its definition varies with the choices of heat and the diffusion flows. Using the Onsager reciprocal relations we can express the heat of transport in terms of the measured thermal diffusion coefficient; it is then possible to obtain experimental values of heats of transport [12, 15]. The experimental technique for measuring the heat of transport is detailed by Rowley et al. [12].

Eqs. (4) and (5) can also be written in terms of the heat of transport and the transport coefficients

$$-\mathbf{J}_q'' = k \nabla T + \rho D Q_1^* \nabla w_1, \quad (10)$$

$$-\mathbf{j}_1 = \rho D_T \nabla \ln T + \rho D \nabla w_1, \quad (11)$$

Where D_T is the thermal diffusion coefficient. The thermal diffusion ratio for substance 1, $K_{T,1}$ is defined in terms of the thermal diffusion coefficient or in terms of the cross-phenomenological coefficient as

$$K_{T,1} = \frac{D_{T,1}}{D} = \frac{L_{1q}}{D\rho} \quad (12)$$

and indicates the level of separation that can be achieved in a steady-state thermal diffusion process.

Dividing Eq. (4) by Eq. (5), and after further dividing both the numerator and denominator by $(L_{qq}L_{11})^{1/2}X_1$

We obtain

$$\eta = \frac{(L_{qq}/L_{11})^{1/2} \lambda + Q_1^* (L_{11}/L_{qq})^{1/2}}{Q_1^* (L_{11}/L_{qq})^{1/2} \lambda + (L_{11}/L_{qq})^{1/2}}. \quad (13)$$

Here we express L_{1q} in terms of the heat of transport Q_1^* : $L_{1q} = Q_1^* L_{11}$, and define the ratio of forces as $\lambda = X_q/X_1$ and the ratio of flows as $\eta = \mathbf{J}_q''/\mathbf{j}_1$. Eq. (13) shows that the ratio of flows η varies with the ratio of forces λ . The ratio

$$r = Q_1^* \left(\frac{L_{11}}{L_{qq}} \right)^{1/2} \quad (14)$$

is known as the degree of coupling, which results from the interference between the forces and the flows, and has been used as a basis for comparison of systems with various coupled forces [4]. The degree of coupling r can be expressed in terms of the transport coefficients by using Eqs. (8) and (14)

$$r = Q_1^* \left(\frac{\rho D M_1 M_2 w_1 w_2}{k M R T^2 (1 + \Gamma_{11})} \right)^{1/2}, \quad (15)$$

where $\Gamma_{11} = (\partial \ln \gamma_1 / \partial \ln x_1)_{T,P}$ is known as the thermodynamic factor, and can be determined from experimental data or an activity coefficient model such as NRTL or UNIFAC. The thermal diffusion ratio K_T can also be expressed in terms of the degree of coupling and the transport coefficients as follows

$$K_{T,1} = r \left(\frac{k M_1 M_2 w_1 w_2}{\rho D M R (1 + \Gamma_{11})} \right)^{1/2}. \quad (16)$$

Eq. (15) shows that r is directly proportional to the heat of transport, and inversely proportional to temperature, and Eq. (16) shows that the thermal diffusion ratio is a function of the degree of coupling. As the heat and diffusion flows are both vectors, the sign of r indicates the direction of flows of a substance. If $r > 0$, the flow of a substance may drag another substance in the same direction, however it may push the other substance in the opposite direction if $r < 0$. For heat and mass flows the dissipation function, Eq. (I), defines the two limiting values of r as $+1$ and -1 . An incomplete coupling takes a value between these two limits [4].

- The phenomenological stoichiometry is defined by the ratio [16]

$$z = \left(\frac{L_{qq}}{L_{11}} \right)^{1/2}. \quad (17)$$

With the definitions of \mathbf{L} and z , Eq. (13) can be written as

$$\eta = \frac{z\lambda + r}{r\lambda + 1/z}. \quad (18)$$

Eq. (18) shows that for a fixed value of z , the ratio of flows depends on the degree of coupling and the ratio of forces. As the degree of coupling approaches zero, the flows become independent, and the ratio of flows approaches $\eta = z^2 \lambda$. If r approaches ± 1 , then the two flows are no longer associated with the forces, and the ratio of flows approaches a fixed ratio $\lambda = \pm z$ [4]. This case is complete coupling where the matrix of the phenomenological coefficients becomes singular, and corresponds to the equality sign in Eq. (7). Negative values of η arise when the derivative of the chemical potential with respect to concentration is negative due to nonideality of the mixture [5]. The degree of coupling is not a unique characteristic of the system since there may be various ways of describing flows and forces consistent with a given dissipation rate. For complete coupling $r = \pm 1$, and z has a unique value.

Using the ratio z , we can define the dimensionless numbers of the reduced force ratio $z\lambda$, and the reduced flow ratio η/z and can relate them by using Eq. (18)

$$\eta/z = \frac{z\lambda + r}{rz\lambda + 1}. \quad (19)$$

Based on the dissipation function equation (I), we can further define the distribution ratio of dissipations due to heat and mass flows in terms of the reduced force ratio and the degree of coupling from Eq. (18) as

$$\eta\lambda = -\frac{\mathbf{J}_q'' X_q}{\mathbf{j}_1 X_1} = -\frac{r + z\lambda}{r + 1/z\lambda}. \quad (20)$$

Eq. (20) has been used as the efficiency of energy conversion in bioenergetics, when $j_1 X_1$ is the input power, and $\mathbf{J}_q'' X_q$ is output [4]. With these definitions, diffusion drives the heat flow and the term $(z\lambda/r)$ changes between 0 and -1. Since $\eta\lambda$ is zero when either \mathbf{J}_q'' or X_q is zero, then it must pass through a maximum at intermediate values. The values of $\eta\lambda$ are often small in regions of physical interest, and the maximum depends on the degree of coupling only [4].

$$(\eta\lambda)_{\max} = \frac{r^2}{(1 + \sqrt{1 - r^2})^2}. \quad (21)$$

For a ternary mixture the phenomenological equations are given by

$$-J_q'' = k\nabla T + \rho(D_{11}Q_1^* + D_{21}Q_2^*)\nabla w_1 + \rho(D_{12}Q_1^* + D_{22}Q_2^*)\nabla w_2, \quad (22)$$

$$-j_1 = \rho D_{T,1}\nabla \ln T + \rho D_{11}\nabla w_1 + \rho D_{12}\nabla w_2, \quad (23)$$

$$-j_2 = \rho D_{T,2}\nabla \ln T + \rho D_{21}\nabla w_1 + \rho D_{22}\nabla w_2, \quad (24)$$

Where D_{ij} is the diffusion coefficient. The two independent heats of transport are related to the two independent cross-phenomenological coefficients L_{q1} and L_{q2} as

follows

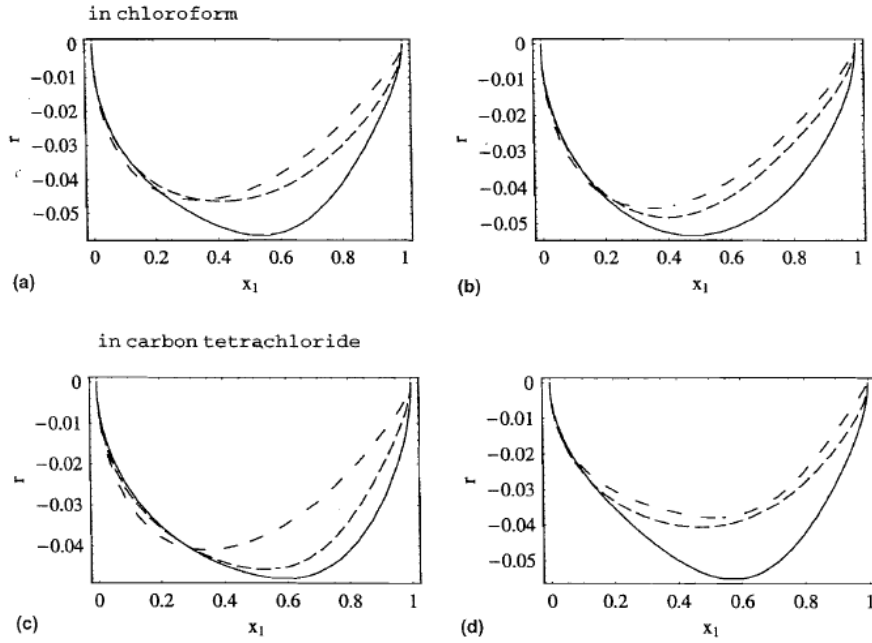


Fig. 1. Change of degree of coupling r with alkane concentration x_1 at 30°C and ambient pressure: (a) straight-chain alkanes: (—) n -hexane, (---) n -heptane, (- - -) n -octane; (b) branched-chain alkanes: (—) 3-methylpentane, (---) 2,3-dimethylpentane, (- - -) 2,2,4-trimethylpentane.

$$L_{q1} = L_{11}Q_1^* + L_{21}Q_2^*, \quad (25)$$

$$L_{q2} = L_{12}Q_1^* + L_{22}Q_2^*. \quad (26)$$

The two independent degrees of coupling between heat and independent diffusions are given by

$$r_{q1} = \frac{L_{q1}}{(L_{qq}L_{11})^{1/2}}, \quad (27)$$

$$r_{q2} = \frac{L_{q2}}{(L_{qq}L_{22})^{1/2}}. \quad (28)$$

Eqs. (27) and (28) show the relationship between the extent of coupling and the cross-phenomenological coefficients. The parameters of Eqs. (15), (16) and (27), (28) will now be determined using experimental data.

Results

The set of binary data for the heat of transport, the thermal conductivity, and the mutual diffusivity coefficients at 25°C, 30°C and 35°C and ambient pressure was taken from Rowley et al. [11,12], and Yi and Rowley [10]. The authors reported error levels of 2% for diffusivities and thermal conductivities, and about 4% for heat of transport measurements. The sign of the heat of transport and the phenomenological coefficients is an artifact of numbering the substances since the $-Q_1^* = Q_2^*$ in a binary mixture of substances 1 and 2. The negative sign with the numbering system used here indicates that heat is transported down the composition gradient of the more concentrated substance [12]. The polynomial fits to the measured transport coefficients are given in Appendix A in Tables 5-10. Since no experimental thermal conductivity for the hexane-carbon tetrachloride mixture has been reported [12], it has been predicted by the local composition model proposed by Rowley [17]. Rowley et al. [11, 12] used the NRTL and UNIFAC models with the data given in DECHEMA series I-1 81- to calculate the thermodynamic factors. We used the same models in this study. However, it should be noted that, the thermodynamic factors obtained from various molecular models as well as two sets of parameters for the same model might be different [19]. Pure component densities are taken from Lide and Kehiaian [20].

The first set of binary liquid mixtures consists of six-to-eight carbon alkanes of n-hexane, n-heptane, n-octane, 3-methylpentane, 2,3-dimethylpentane, and 2,2,4-trimethylpentane in chloroform and in carbon.

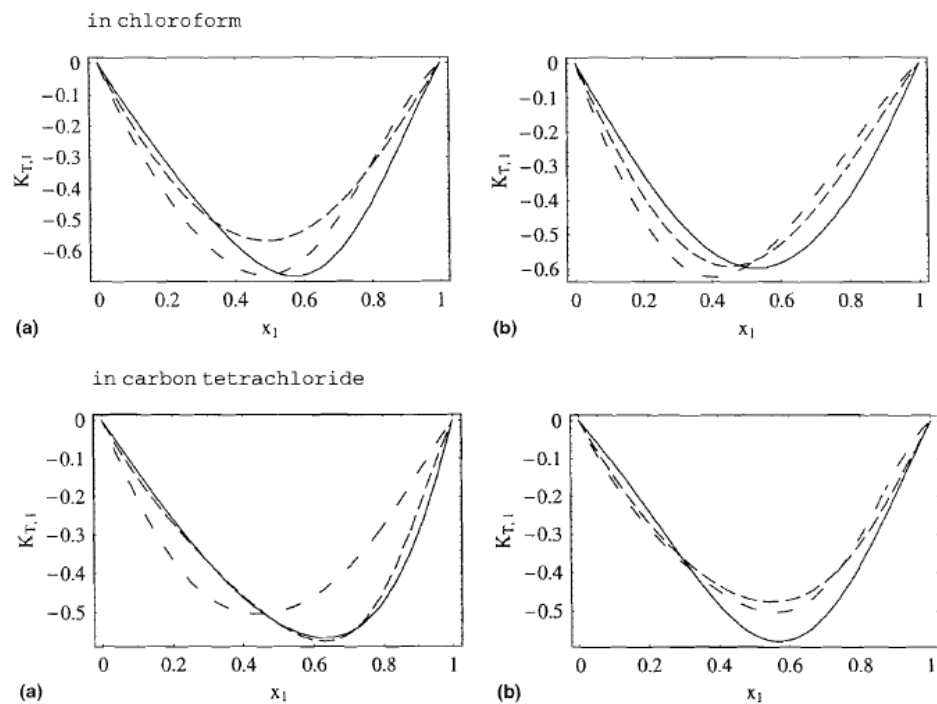


Fig. 2. Change of thermal diffusion ratio $K_{T,1}$ with alkane concentration x_1 at 30°C and ambient pressure: (a) straight-chain alkanes: (—) *n*-hexane, (---) *n*-heptane, (- - -) *n*-octane; (b) branched-chain alkanes: (—) 3-methylpentane, (---) 2,3-dimethylpentane, (- - -) 2,2,4-trimethylpentane.

Table 1
Degree of coupling r , and maximum ratio of dissipation $(\eta\lambda)_{\max}$

Straight-chain alkanes				Branched-chain alkanes			
Solute	$-r_{\max}$	x_1^*	$(\eta\lambda)_{\max} \times 10^4$	Solute	$-r_{\max}$	x_1^*	$(\eta\lambda)_{\max} \times 10^4$
(a) For alkanes in chloroform				3-methylpentane	0.0532	0.475	7.085
<i>n</i> -hexane	0.0565	0.534	7.993	2,3-dimethylpentane	0.0482	0.392	5.815
<i>n</i> -heptane	0.0463	0.408	5.365	2,2,4-trimethylpentane	0.0457	0.340	5.226
<i>n</i> -octane	0.0460	0.337	5.295				
(b) For alkanes in carbon tetrachloride				3-methylpentane	0.0550	0.570	7.574
<i>n</i> -hexane	0.0478	0.588	5.718	2,3-dimethylpentane	0.0404	0.467	4.083
<i>n</i> -heptane	0.0456	0.527	5.203	2,2,4-trimethylpentane	0.0378	0.513	3.574
<i>n</i> -octane	0.0409	0.341	4.185				

x_1^* : concentration at maximum r .

Table 2
Thermal diffusion ratio for solute $K_{T,1}$

Straight-chain alkanes			Branched-chain alkanes		
Solute	$-K_{T,1}$	x_1^*	Solute	$-K_{T,1}$	x_1^*
(a) For alkanes in chloroform			3-methylpentane	0.596	0.527
<i>n</i> -hexane	0.679	0.569	2,3-dimethylpentane	0.591	0.449
<i>n</i> -heptane	0.565	0.488	2,2,4-trimethylpentane	0.622	0.402
<i>n</i> -octane	0.675	0.484			
(b) For alkanes in carbon tetrachloride			3-methylpentane	0.579	0.569
<i>n</i> -hexane	0.564	0.629	2,3-dimethylpentane	0.476	0.550
<i>n</i> -heptane	0.572	0.628	2,2,4-trimethylpentane	0.503	0.557
<i>n</i> -octane	0.503	0.441			

x_1^* : concentration at maximum $K_{T,1}$.

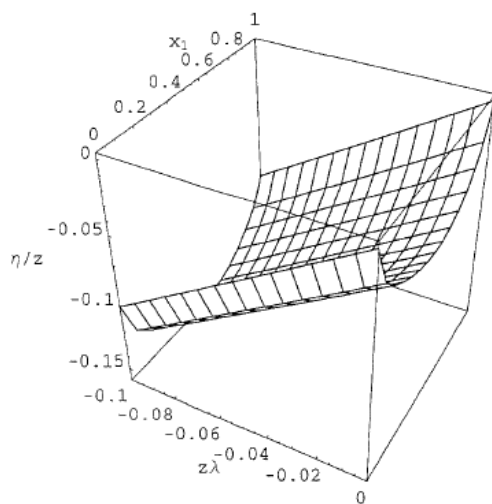


Fig. 3. A typical surface of the reduced flow ratio η/z in terms of the reduced force ratio $z\lambda$ and *n*-hexane concentration x_1 in chloroform at 30°C and ambient pressure.

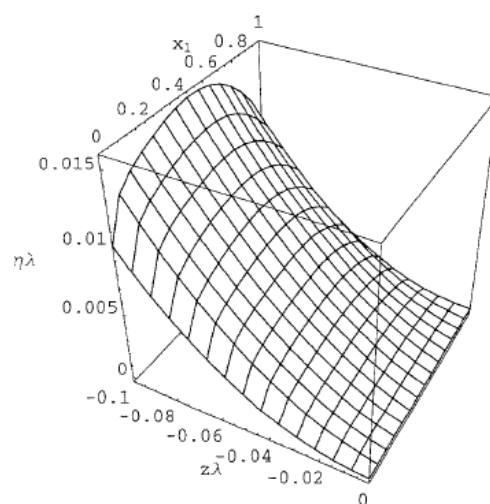


Fig. 4. A typical surface of the dissipation ratio $\eta\lambda$ in terms of the reduced force ratio $z\lambda$ and *n*-hexane concentration x_1 in chloroform at 30°C and ambient pressure.

Tetrachloride. Rowley et al. [11, 12] reported that in- creasing chain length decreases the diffusivity and heat of transport, and has only marginal effect on thermal conductivity.

As the degree of coupling depends on the complete set of heat and mass transfer coefficients, a plot of r versus alkane concentrations, \mathbf{X}_1 shows the combined effect of the transport coefficients on r with changing concentrations and temperatures. The degree of coupling r between heat and mass flows and the thermal diffusion ratio $K_{T,1}$ are calculated for the full compo-

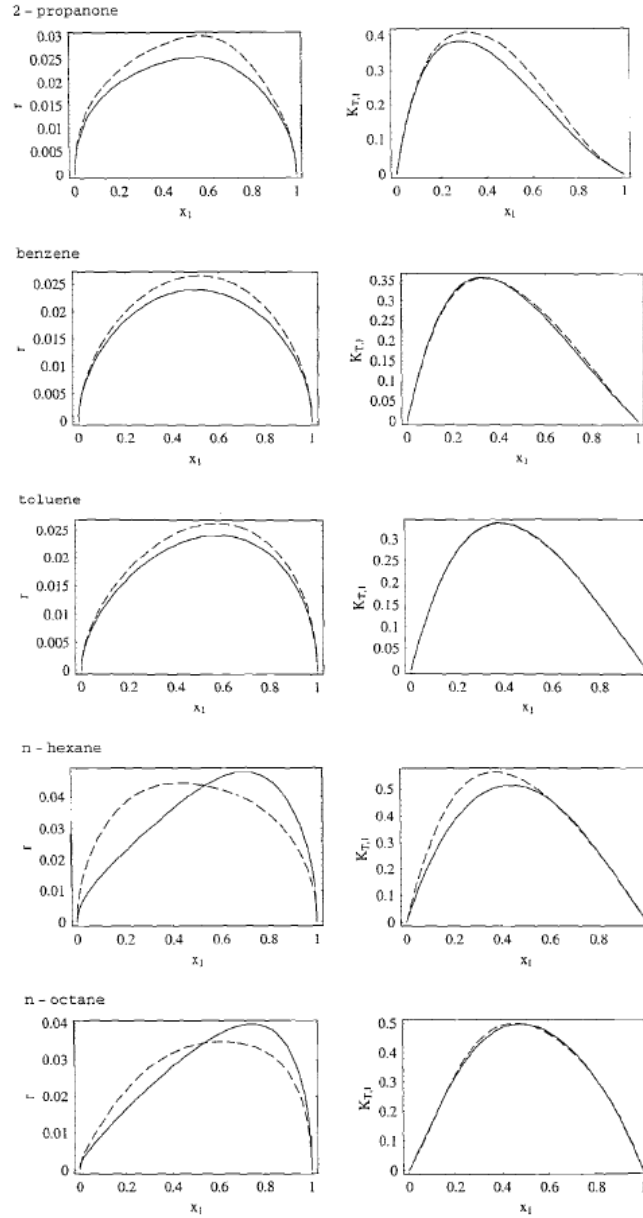


Fig. 5. Change of degree of coupling r and thermal diffusion ratio $K_{T,1}$ for carbon tetrachloride (1) in solvents: 2-propanone, benzene, toluene, n -hexane, n -octane at 25°C (—), and at 35°C (---) and ambient pressure.

sition range from Eqs. (15) and (16), and are shown in Figs. 1 and 2 respectively. These show four important properties of coupling. (i) The absolute values of r and $K_{T,I}$ reach maximum values at an intermediate concentration of alkane, and these peak values generally decrease gradually as the molecular weight increases. (ii) The solute concentrations at maximum r and $K_{T,I}$ decrease gradually as the molecular weights increase. These effects have been summarized in Tables 1 and 2. (iii) The behavior of all the alkanes with increasing concentration is similar up to approximately $x_1 = 0.2$, but depending upon the combined effect of branching and solvent on r , though at higher concentrations they behave differently. (iv) The absolute maximum extent of coupling is small as expected, and the branching has only a marginal effect.

In Tables 1 and 2, the values of r and $K_{T,I}$, and the concentrations at which the absolute maxima occur, are shown for both the straight and branched alkanes in both chloroform and in carbon tetrachloride. The tables also show the effect of the solvent on r and $K_{T,I}$. The alkane concentrations at the maxima of r and $K_{T,I}$ are generally lower in chloroform than in carbon tetrachloride, the peak values of r and $K_{T,I}$ are higher. Table 1 also shows the change of maximum values of dissipation ratio $(\eta\lambda)_{max}$ with the concentration of the solutes in chloroform and in carbon tetrachloride. The maximum values of $\eta\lambda$ decrease with increasing molecular weight in both the solvents.

Figs. 3 and 4 display the calculated surfaces of the reduced flow η/z and the dissipation ratio $\eta\lambda$, in terms of the reduced force ratio $z\lambda$ in the range -0.1-0, for various hexane concentrations x_i in chloroform. The effect of hexane concentration on η/z remains the same as $z\lambda$ changes from -0.1 to 0, while the surface of the dissipation ratio $\eta\lambda$ changes from a curved to a flat shape as $z\lambda$ changes from -0.1 to 0.

The second set of binary liquid mixtures consists of carbon tetrachloride with benzene, toluene, 2-propane, n-hexane, and n-octane at two temperatures and ambient pressure. These represent the systems of carbon tetrachloride with the aromatic rings, a ketone, and the long, straight-chain alkanes. The heat of transport increases with temperature for the aromatics and the ketone, while it decreases slightly for the alkanes. The degree of coupling between heat and mass flows and the thermal diffusion ratio $K_{T,I}$ are shown in Fig. 5 for 2-propane, the aromatics and the alkanes at two temperatures of 25°C and 35°C. The peak values of r decrease with increasing molecular weight, and the extent of coupling r increases with temperature for the aromatics and 2-propanone, while it decreases for the alkanes.

The groups of 2-propanone and the aromatics, and the groups of alkanes show distinctive behavior. The extent of coupling is higher in the alkanes than in 2-propanone and the aromatics. This might be because of the shape of the molecules considered. The solute concentrations at the peak values decrease for the alkanes, and increase slightly for the aromatics as the molecular weights increase. Temperature has relatively larger effect on the coupling of the alkanes than on the aromatics and 2-propanone. Changing temperatures from 25°C to 30°C decreases the concentration of carbon tetrachloride at the peak values of r and $K_{T,I}$ for the alkanes. These effects have been summarized quantitatively in Tables 3 and 4. Table 3 shows that the maximum values of $\eta\lambda$ decrease with increasing molecular weight, and increase with temperature for the aromatics and 2-propanone, while they decrease for the alkanes. Generally the maximum values of r and $K_{T,I}$ are relatively larger in the alkanes than in the aromatics and 2-propanone. These

results demonstrate how concentration, molecular weight, chain length, and temperature affect the level of coupling in binary liquid mixtures.

For the ternary mixture of toluene(1)-chlorobenzene(2)- bromobenzene(3), the set of data for the heat of transport, the thermal conductivity, and the mutual

Table 3
Degree of coupling r , and maximum ratio of dissipation $(\eta\lambda)_{\max}$ for the systems of carbon tetrachloride (1) in various solvents

Solvent	M	T (K)	r_{\max}	x_1^*	$(\eta\lambda)_{\max} \times 10^3$
2-propanone	58.081	298.15	0.0254	0.543	0.161
		308.15	0.0300	0.564	0.226
benzene	78.114	298.15	0.0240	0.503	0.144
		308.15	0.0265	0.519	0.176
toluene	92.141	298.15	0.0236	0.539	0.139
		308.15	0.0257	0.539	0.166
<i>n</i> -hexane	86.178	298.15	0.0478	0.699	0.573
		303.15	0.0444	0.428	0.493
<i>n</i> -octane	114.232	298.15	0.0397	0.744	0.395
		303.15	0.0349	0.612	0.306

x_1^* : concentration at maximum r .